

Ambient pressure photoemission spectroscopy reveals the mechanism of carbon soot oxidation in ceria-based catalysts

Lluís Soler,^[a] Albert Casanovas,^[a] Carlos Escudero,^[b] Virginia Pérez-Dieste,^[b] Eleonora Aneggi,^[c] Alessandro Trovarelli,^[c] Jordi Llorca,^{*,[a]}

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- [a] Dr. L. Soler, Dr. A. Casanovas, Prof. J. Llorca
Institute of Energy Technologies and Centre for Research in Nanoengineering
Universitat Politècnica de Catalunya
Diagonal 647, ed. ETSEIB, 08028 Barcelona, Spain
E-mail: jordi.llerca@upc.edu
- [b] Dr. C. Escudero, Dr. V. Pérez-Dieste
ALBA Synchrotron Light Source
Carrer de la Llum 2-26, 08290 Cerdanyola del Vallès, Barcelona, Spain
- [c] Dr. E. Aneggi, Prof. A. Trovarelli
Dipartimento Politecnico
Università di Udine
Via del Cotonificio 108, IT-33100 Udine, Italy

Abstract: Removing soot is one of the most important challenges in minimizing the impact of combustion engines on the environment. Catalysts based on CeO₂ have proved suitable to oxidize soot due to their capacity to store and release oxygen easily while maintaining structural integrity, although their mode of operation in a complex environment involving two solid phases (catalyst and soot) and a gas phase (oxygen) is not yet fully understood. Here we provide a study of the surface/subsurface of ceria-soot and ceria-zirconia-soot mixtures under working conditions by means of near ambient pressure photoelectron spectroscopy. Soot abatement involves two cooperative routes: one occurring at the ceria-soot interface with formation of oxygen vacancies and Ce^{III}, and another at the surface of soot mediated by active superoxide species, which result from the reaction between gas-phase O₂ and oxygen vacancies. The two routes occur simultaneously and mutually reinforce each other.

Soot elimination constitutes a serious environmental and health concern as soot particles are undesired by-products formed in combustion processes and emitted as a main pollutant from diesel engines. Usually, particle traps are used for soot removal and, in order to avoid filter blocking, effective regeneration systems have been developed to oxidize soot. Thermal combustion of soot usually requires temperatures above 600°C, and catalysts play a key role in lowering the ignition temperature. Ceria-based catalysts are among the most effective for diesel soot oxidation^[1] and incorporation of Zr and rare earth elements, particle morphology and ceria-soot interface have been demonstrated to be strongly involved in the dynamics of the reaction.^[2] It has been generally assumed that soot oxidation proceeds via a Mars-Van Krevelen mechanism. That is, lattice oxygen in the first few surface layers of ceria is transferred onto soot, and gaseous O₂ fills up the vacancies created on the oxide in a further step.^[3] However, the mechanism of action has also been associated with the availability of adsorbed active oxygen species which spillover onto the soot

surface.^[3a,4] Formation of paramagnetic O_2^- superoxide species and diamagnetic O_2^{2-} peroxide species has been claimed to occur when reduced CeO_{2-x} is exposed to O_2 ,^[5] and it has been suggested that these are indeed the precursor surface species which are responsible for soot oxidation.^[3a,6] In the present study, we use *operando* ambient pressure X-ray photoelectron spectroscopy (AP-XPS) for the first time to study the surface of CeO_2 and $Ce_{0.8}Zr_{0.2}O_2$ catalysts during soot oxidation. AP-XPS is a unique surface-sensitive characterization tool essential to identify the active species at work in reducible oxides such as ceria-based materials, as the surface restructuring driven by the reaction environment induces strong changes in their architecture that cannot be followed under UHV conditions.^[7]

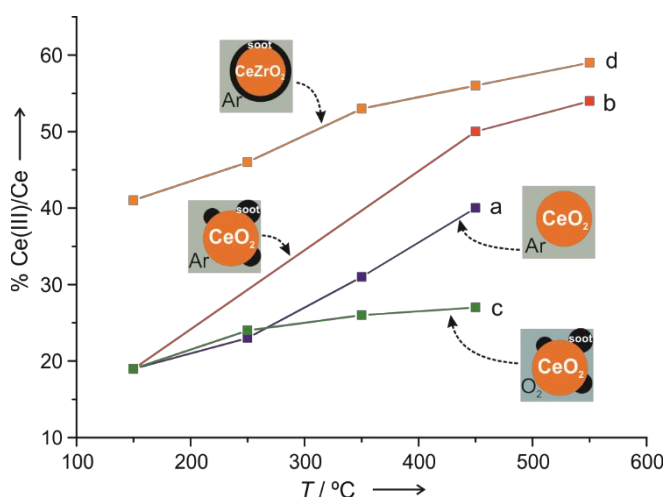


Figure 1. Amount of reduced ceria measured at different temperatures in bare CeO_2 under Ar (a), in sample CeO_2 -soot under Ar (b), in sample CeO_2 -soot under O_2 (c), and in sample $Ce_{0.8}Zr_{0.2}O_2$ -soot under Ar (d).

A sample of conventional ceria and a sample of $Ce_{0.8}Zr_{0.2}O_2$ mixed with soot were investigated in this study. A sample of ceria without soot was used as blank. The mixing of the catalysts with carbon soot (weight ratio catalyst:soot of 20:1) was accomplished under conventional tight contact mode for CeO_2 ^[8] and under supertight contact achieved by high-energy milling of $Ce_{0.8}Zr_{0.2}O_2$ and soot for 8h.^[2b] Both materials crystallize in a cubic fluorite structure and exhibit similar surface area and particle size (Table S1). Soot clumps are easily recognized in the HRTEM images of the CeO_2 -soot sample, whereas high-energy milling of $Ce_{0.8}Zr_{0.2}O_2$ and soot results in the formation of a core of oxide particles wrapped in a thin carbon envelope (Figure S1), in accordance with

earlier reports.^[2b,8] This greatly increases the number and quality of contact points between the catalyst and carbon, shifting the combustion of soot to exceptionally low temperatures (Table S1).

Three *operando* AP-XPS experiments (ALBA synchrotron light source) were carried out at 1 mbar over CeO₂: (i) heating CeO₂ from room temperature up to 450°C under Ar, to be used as blank experiment, (ii) heating the CeO₂-soot mixture from room temperature up to 550°C under Ar and then replacing Ar with O₂, and (iii) heating the CeO₂-soot mixture from room temperature up to 550°C under O₂. It is well known that heating CeO₂ under inert atmosphere causes the formation of oxygen vacancies and the concomitant reduction of Ce^{IV} to Ce^{III}.^[9] As expected, Ce^{III} increased with temperature (Figures 1a and S2). However, in the presence of soot, ceria reduction was significantly higher (Figures 1 and 2), which means that ceria lattice oxygen atoms directly react with soot, in accordance with the Mars-Van Krevelen mechanism and with previous reports.^[10] This observation is also supported by the progressive decrease of the C/Ce atomic ratio as the temperature increases (C/Ce=24.4 at 450°C vs. 16.0 at 550°C).

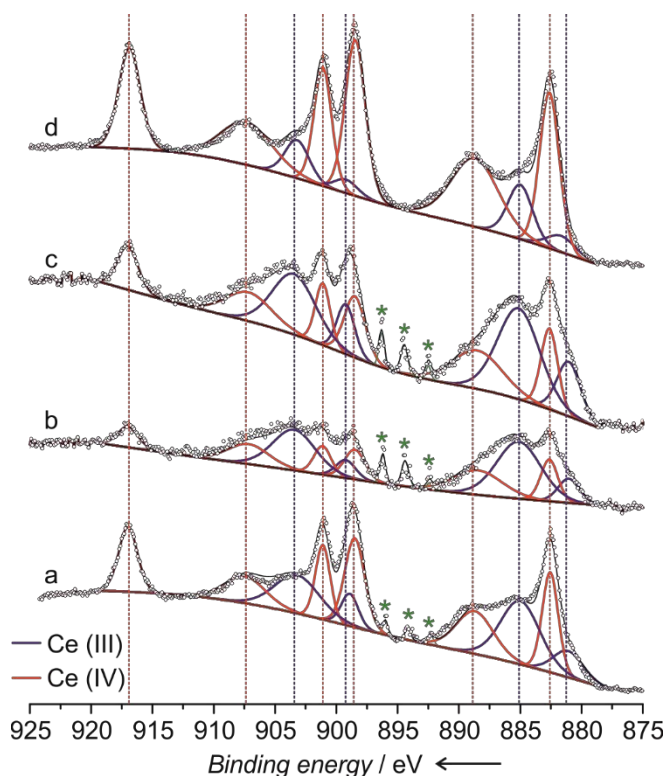


Figure 2. Ce 3d spectra recorded over CeO₂ under Ar at 450°C (a) and over CeO₂-soot under Ar at 450°C (b), 550°C (c) and by replacing Ar with O₂ at 550°C (d). (★Ar gas phase).

At 550°C, Ar was replaced with O₂ and, as expected, Ce^{III} reoxidized to Ce^{IV} to a large extent (Figure 2d), reducing the total amount of Ce^{III} from ca. 50 to 16%. The introduction of oxygen on a heavily reduced ceria surface results, not only in the reoxidation of Ce^{III}, but also in a deep oxidation of residual soot (C/Ce from 16 to 2.9). Under Ar, the O 1s signal recorded at 528.7 eV (Figure 3a) corresponds to ceria lattice oxygen, and the minor contribution at 530.7 eV is ascribed to different ceria lattice oxygen environments upon vacancy formation.^[11] It should be mentioned that, in the presence of soot (Figure 3b), there is a broadening of the O 1s signal at high binding energies with respect to the spectrum of bare CeO₂ (Figure 3a), pointing to a variety of surface/subsurface oxygen environments, which can be directly related with the higher amount of Ce^{III} in the CeO₂-soot sample (bare soot showed an O/C ratio of only ~0.04, thus the contribution of soot to the O 1s signal is negligible). Upon contact with oxygen, in addition to the peaks at 538.6 and 537.5 eV corresponding to paramagnetic O₂ in the gas phase,^[12] two peaks at 530.5 and 532.2 eV appeared (Figure 3c). According to literature, these peaks are attributed to peroxide (O₂²⁻) and superoxide (O₂⁻) species, respectively.^[13]

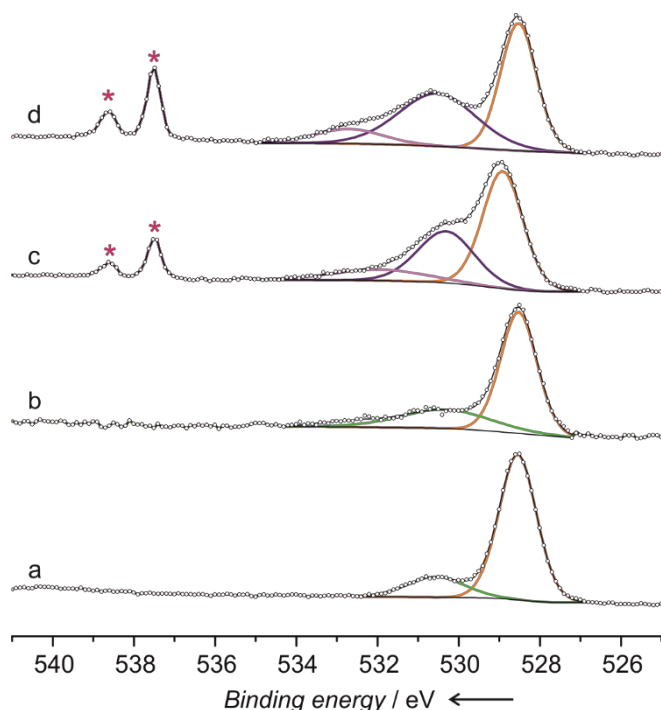
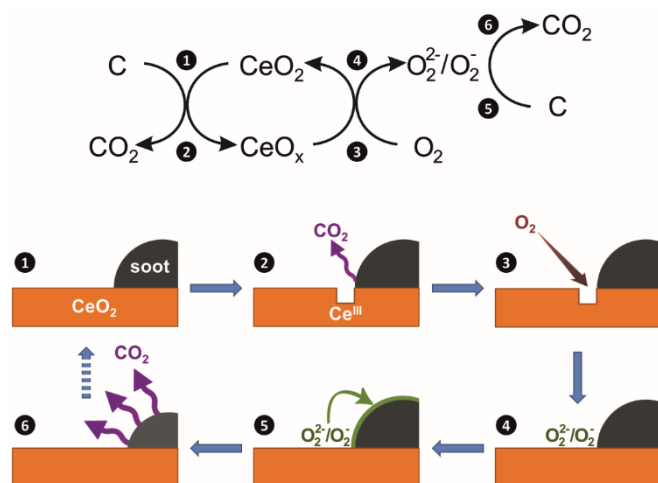


Figure 3. O 1s spectra recorded over CeO₂ under Ar at 450°C (a) and over CeO₂-soot at 550°C under Ar (b) and by replacing Ar with O₂ at 550°C (c). Spectrum (d) corresponds to the CeO₂-soot sample heated directly under O₂ from ambient temperature. (★O₂ gas phase).

In a separate experiment, the CeO₂-soot sample was heated from room temperature up to 550°C under O₂ (Figure 1c and Figure S3). In this case, the amount of Ce^{III} species remained low over the entire temperature range, indicating that the oxygen vacancies created at the ceria-soot interface reacted rapidly with O₂, as expected. As outlined above, the reaction between molecular O₂ and the oxygen vacancies form active oxygen species (O₂²⁻ and O₂⁻),^[14] which were clearly seen in the O 1s spectra of the experiment carried out under O₂ (Figure 3d). The amount of O₂⁻ species observed in the experiment performed under Ar and then switched to an oxygen atmosphere was lower than that recorded in the experiment under O₂ (O₂²⁻/O₂⁻=16.4 vs. 4.8), which might indicate a higher reactivity of the superoxide species toward soot oxidation than that of the peroxide species.



Scheme 1. Scheme of the mechanism of soot oxidation over ceria-based catalysts. 1-Reaction between soot and ceria at the contact points. 2-Formation of oxygen vacancies at the interface and release of CO₂. 3-Reaction between O₂ and oxygen vacancies. 4-Reoxidation of ceria surface and formation of active oxygen species (O₂⁻ and O₂²⁻). 5-Spillover of active oxygen species onto soot. 6-Reaction between soot and active oxygen species and release of CO₂. The cycle starts over again at the new contact points between soot and ceria until soot is completely oxidized.

Our AP-XPS results support a mechanism where ceria is first reduced by soot at the interface between the carbon particles and the ceria surface releasing CO₂, and then the reduced ceria surface reacts with gaseous oxygen refilling the oxygen vacancies and yielding peroxide/superoxide species. These active oxygen species likely migrate to the carbon surface and react efficiently to form CO₂ at a much lower energy cost. Then, a new contact point between soot and the surface of ceria is established and the cycle starts over again (Scheme 1). To further validate this scheme, we studied Ce_{0.8}Zr_{0.2}O₂-soot mixed under supertight conditions, which showed an extraordinary low soot

combustion temperature (Table S1).^[2b] The amount of Ce^{III} upon heating under Ar was, in all cases, higher than that recorded over the CeO₂-soot sample (Figures 1b, 1d, 4a, and S4). The O 1s spectrum recorded under Ar showed three components at 528.7, 530.2 and 532.2 eV (Figure 4c). The peaks at 528.7 and 530.2 eV correspond to lattice oxygen and surface oxide ions with low coordination resulting from vacancy formation, respectively. The peak at 532.2 eV, attributed to superoxide species, was extraordinarily intense. At 550°C, the Ar atmosphere was replaced with O₂ and the amount of Ce^{III} immediately decreased from ca. 60% to 23.5% (Figure 4b). At the same time, the O 1s peak of surface oxide ions with low coordination associated to Ce^{III} present at the surface/subsurface (at 530.2 eV) decreased due to the reoxidation of ceria (Figure 4d). In addition, the superoxide signal at 532.1 eV dominated the spectrum and the O/Ce ratio increased from 17.4 to 23.2, **in agreement with FTIR and EPR measurements of previous reports,^[15]** thus supporting the idea that the superoxide O₂⁻ species formed by reaction between molecular O₂ and oxygen vacancies redistributed on the catalyst surface.

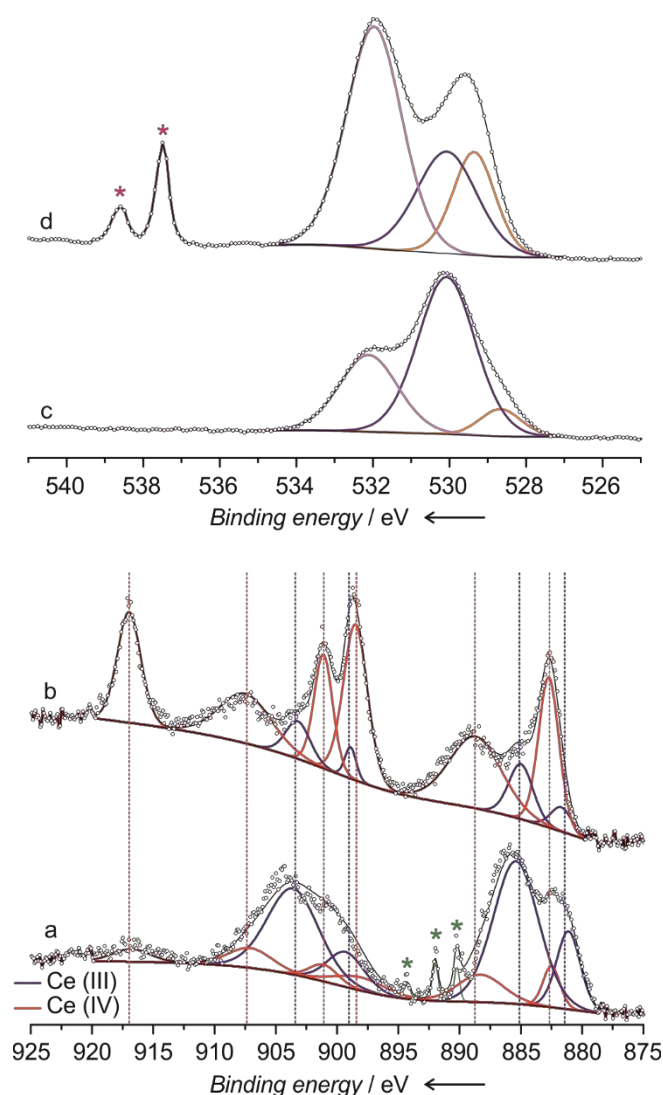


Figure 4. Ce 3d and O 1s spectra recorded over $\text{Ce}_{0.8}\text{Zr}_{0.2}\text{O}_2$ -soot at 550°C under Ar (a,c) and by replacing Ar with O_2 (b,d). (green★, Ar gas phase; pink★, O_2 gas phase).

We have provided by AP-XPS a direct measurement of the unique behaviour of the $\text{Ce}^{\text{III}}/\text{Ce}^{\text{IV}}$ redox chemistry and the influence of the reaction environment in the oxidation of carbon soot over ceria-based catalysts. The AP-XPS technique demonstrates the capacity of ceria to oxidize soot owing to the formation of oxygen vacancies with reduction of Ce^{IV} to Ce^{III} , and the significant formation of active oxygen surface species due to the reaction of oxygen vacancies and molecular O_2 . A general two-way cooperative mechanism of soot oxidation over ceria-based materials has been therefore demonstrated, providing reliable information on the local characteristics of the surface/subsurface species involved in this complex heterogeneous solid/solid/gas catalytic process.

Experimental Section

CeO₂ and Ce_{0.8}Zr_{0.2}O₂ were prepared by precipitation of an acidic solution of nitrate precursors with NH₄OH in presence of H₂O₂. AP-XPS experiments were carried out at the CIRCE beamline of the ALBA synchrotron light source at a sample pressure of 1 mbar. A full description of the methodology is given in the SI.

Acknowledgements

This work has been funded through MINECO grant ENE2015-63969-R. L.S. is grateful to Generalitat de Catalunya for a Beatriu de Pinós grant (2013 BP-B 00007). J.L. is Serra Húnter Fellow and is grateful to ICREA Academia program. E.A. and A.T. are grateful to regione Friuli Venezia Giulia. The AP-XPS experiments were performed at CIRCE beamline at ALBA Synchrotron with the collaboration of ALBA staff.

Keywords: Soot combustion • ceria catalysts • near ambient pressure photoelectron spectroscopy • oxygen storage • heterogeneous catalysis

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